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Uranium and Aluminosilicate Surface Precipitation Tests

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Nuclear Science and Technology Division

URANIUM AND ALUMINOSILICATE SURFACE PRECIPITATION TESTS

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ACRONYMS AND NOMENCLATURE

BSE	back-scattering electron
EDS	energy dispersion spectroscopy
ICP-AES	inductively coupled plasma (atomic emission spectroscopy)
NAS	sodium aluminosilicate
SE	secondary electron imaging
SEM	scanning electron microscopy
SRS	Savannah River Site
SRTC	Savannah River Technology Center
XRD	X-ray diffraction

EXECUTIVE SUMMARY

The 2H evaporator at the Savannah River Site has been used to treat an aluminum-rich waste stream from canyon operations and a silicon-rich waste stream from the Defense Waste Processing Facility. The formation of aluminosilicate scale in the evaporator has caused significant operational problems. Because uranium has been found to accumulate in the aluminosilicate solids, the scale deposition has introduced criticality concerns as well. The objective of the tests described in this report is to determine possible causes of the uranium incorporation in the evaporator scale materials. The scope of this task is to perform laboratory experiments with simulant solutions to determine if (1) uranium can be deposited on the surfaces of various sodium aluminosilicate (NAS) forms and (2) aluminosilicates can form on the surfaces of uranium-containing solids.

Batch experiments with simulant solutions of three types were conducted: (1) contact of uranium solutions/sols with NAS coatings on stainless steel surfaces, (2) contact of uranium solutions with NAS particles, and (3) contact of precipitated uranium-containing particles with solutions containing aluminum and silicon. The results show that uranium can be incorporated in NAS solids through encapsulation in bulk agglomerated NAS particles of different phases (amorphous, zeolite A, sodalite, and cancrinite) as well as through heterogeneous deposition on the surfaces of NAS coatings (amorphous and cancrinite) grown on stainless steel. The results also indicate that NAS particles can grow on the surfaces of precipitated uranium solids. Particularly notable for evaporator operations is the finding that uranium solids can form on existing NAS scale, including cancrinite solids. If NAS scale is present, and uranium is in sufficient concentration in solution to precipitate, a portion of the uranium can be expected to become associated with the scale.

The data obtained to date on uranium–NAS affinity are qualitative. A necessary next step is to quantitatively determine the amounts of uranium that may be incorporated into NAS scale solids under differing conditions e.g., varying silicon/aluminum ratio, uranium concentration, temperature, and deposition time).

1. INTRODUCTION

The 2H evaporator at the Savannah River Site (SRS) has been used to treat an aluminum-rich waste stream from canyon operations and a silicon-rich waste stream from the Defense Waste Processing Facility. In 1997, the gravity drain line from the 2H evaporator became plugged with solids comprising sodium aluminosilicate (NAS) and sodium diuranate. At that time, the sodium diuranate did not pose a criticality concern.[1] In 1999, the evaporator operations were suspended because of poor performance, and a subsequent inspection showed solids on all exposed interior surfaces. Because the amount of ^{235}U in these deposits was a criticality concern,[2] the evaporator was shut down and cleaned. The processes of crystallization and solid deposit formation that led to the shutdown of the 2H evaporator at SRS and that could possibly cause similar problems in the future or in other evaporators need to be more completely understood. A particular need is to determine the fate of the uranium in the evaporator system: material balances of the 2H evaporator have indicated that only a small fraction of the silicon fed to the evaporator was deposited in the evaporator as scale, while the majority of the uranium fed to the evaporator was associated with the scale.[3]

1.1 OBJECTIVE

The objective of the work described in this report is to determine possible causes of uranium incorporation in the evaporator scale materials. This task complements other silicon processing studies[4] being performed at Savannah River Technology Center (SRTC).

1.2 SCOPE

This task involved laboratory experiments with simulant solutions to determine if (1) uranium from such solutions can be deposited on the surface of various NAS forms (suspended particles and films on stainless steel surfaces) and (2) aluminosilicate can form on the surfaces of suspended sodium diuranate particles.

- In the first type of test, samples of stainless steel were coated with aluminosilicates of various phases (i.e., amorphous, zeolite A, sodalite, cancrinite). The samples were contacted with uranium-containing simulant solution and then analyzed for morphology, crystalline phases, and the presence of uranium. Particles of various pure NAS forms were also contacted with the uranium solutions to determine the possibility for growth of uranium-containing solids on the surface of NAS particles.
- In the second type of test, uranium-containing simulant solutions were prepared and aged to precipitate uranium solids. The solutions were then spiked with known concentrations of aluminum and silicon and held at elevated temperature to determine if NAS solids could form on the surface of the uranium solids.

1.3 EXPECTED BENEFITS

The results may provide information on the possible mechanisms by which uranium is concentrated in the aluminosilicate solids. This may be of particular value if these mechanisms can be eliminated by controlling processing conditions.

1.4 BACKGROUND

As part of R&D efforts in support of long-term silicon processing in high-level-waste tank farms,[4] SRTC researchers identified eight types of tests aimed at criticality prevention in evaporator systems during NAS formation.[5] The objective of these tests is to investigate possible means of uranium accumulation in the NAS chain, from amorphous materials to cancrinite in order to determine the mechanisms and quantities of uranium accumulation. It was postulated that an understanding of the mechanisms of uranium accumulation may identify evaporator processing conditions that will minimize uranium accumulation in scale and thus eliminate criticality concerns.

SRTC researchers have postulated the following potential interactions of uranium with aluminosilicate materials[4]:

- sorption of uranium on NAS, facilitating nucleation of uranium solid phases;
- coprecipitation of uranium within NAS structures;
- growth of uranium solids on NAS solids;
- growth of NAS solids on uranium solids; and
- precipitation of uranium as U(VI) oxide, oxide hydrate, or silicate.
-

The following eight tests were identified for investigation of the above mechanisms[5]:

1. sorption studies with uranium on NAS solids;
2. sorption studies with uranium on NAS solids during solid-phase transformations;
3. measurement of growth of uranium solid phases on NAS solids;
4. measurement of growth of NAS solid phases on uranium solids;
5. coprecipitation tests with U, Na, Al, and Si present;
6. coprecipitation tests with U, Na, and Si present—no Al
7. examination of uranium solubility in silicon sols/gels; and
8. analysis of samples from the 2H evaporator pot.

The tasks and results described below address tests 3 and 4; a subset of the remaining tests were conducted by SRTC researchers in FY 2002.

2. EXPERIMENTAL APPROACHES AND PROCEDURES

2.1 APPROACHES

Laboratory experiments with simulant solutions were conducted to determine (1) whether uranium from simulant solution can be deposited onto surfaces of various preexisting NAS forms and (2) whether aluminosilicate can form on the surfaces of suspended sodium diuranate particles.

2.2 DESCRIPTION OF EXPERIMENTAL PROCEDURE

These tests consist of four elements: preparation of coupons with NAS films of various phases, contact of uranium solutions/sols with NAS coatings, contact of uranium solutions with NAS particles, and analysis of solid samples.

2.2.1 Growth of Uranium on NAS

2.2.1.1 Uranium-containing simulant solutions

The background simulant solution consisted of the following components: 6 *M* Na^+, 4.0 *M* OH^-, 1.0 *M* NO_3^-, and 1.0 *M* NO_2^-. Typically, 0-, 25-, and 50-ppm uranium solutions were prepared. When used for exposure to NAS solids (particles or coatings), the solutions were initially contacted with the NAS of corresponding phases (amorphous, zeolite, sodalite, or cancrinite). The equilibrium NAS (silicon and aluminum) concentration of each phase in such background solution was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES.

NAS powders were contacted with simulant solution to approach saturation of the solutions with respect to those phases to minimize dissolution of NAS in the experiments. The different NAS powders were obtained from Dr. Addai-Mensah, University of South Australia.[6] In order to assess the solubility of these powders when placed in the SRS blank solution (3.8 *M* NaOH + 1 *M* $NaNO_3$ + 1 *M* $NaNO_2$ + 0.1 *M* Na_2CO_3), an experiment was conducted at room temperature. Known amounts of NAS solids (zeolite A, amorphous aluminosilicate, nitrated sodalite, nitrated cancrinite, or gibbsite) were introduced into centrifuge tubes, followed by the addition of 45 mL of the SRS blank solution. The vials were manually shaken to mix the powder and the solution and then placed in a vial holder at room temperature for 24 h. After 24 h, the vials were visually inspected to determine whether all the powders were dissolved. A 200-µL sample was withdrawn from each tube for ICP-AES analysis. Addition of NAS followed by ICP-AES analyses was performed over several days, and the results are presented in Table 2.1. These data were used in subsequent experiments to prepare solutions nearly presaturated with NAS of corresponding phases.

2.2.1.2 Growth of Uranium on NAS Particles

These tests involved the contacting of uranium-containing solution with NAS particles of various phases. One of the three triplicate tubes used in the solubility tests described above was used to provide the nearly saturated solution containing aluminum and silicon. After the first 24-h contact, the vial with the largest quantity of solids left on the bottom was selected for each form of NAS. For zeolite A, this corresponded to the solution containing 213 mg/L of aluminum and 212 mg/L of silicon (experimental value), which was achieved by adding 0.098 g of zeolite A to 45 mL of the SRS blank solution. For the amorphous NAS, 0.049 g of solids provided a concentration of 124 mg/L of aluminum and 120 mg/L of silicon. The corresponding sodalite solution was obtained by adding 0.049 g of solids to SRS blank solution, achieving an aluminum concentration of 139 mg/L, and a silicon concentration of 133 mg/L. For cancrinite, 0.104 g of

Table 2.1. ICP-AES results (mg/L) obtained after additions of the NAS compounds to the SRS blank solution

	04-29		04-30		05-01		05-02		05-06		05-09	
	[A1-1]	[Si-1]	[A1-2]	[Si-2]	[A1-3]	[Si-3]	[A1-4]	[Si-4]	[A1-5]	[Si-5]	[A1-6]	[Si-6]
Zeolite A	95	95	256	258	265	268	322	333	421	412	427	436
	48	46	276	280	288	292	342	354	427	431	452	465
	213	212	–	–	–	–	–	–	–	–	–	–
Amorphous	93	90	196	193	199	197	235	236	298	292	295	293
NAS	86	83	265	262	270	267	324	326	396	389	379	378
	124	120	–	–	–	–	–	–	–	–	–	–
Sodalite	101	96	214	209	201	196	245	244	278	268	274	267
	159	153	294	287	266	261	291	291	331	321	319	313
	139	133	–	–	–	–	–	–	–	–	–	–
Cancrinite	26	23	57	52	41	38	45	43	58	51	59	55
	23	19	55	48	41	37	46	44	59	52	60	56
	31	28	–	–	–	–	–	–	–	–	–	–
Gibbsite	337	–	555	–	609	–	738	–	980	–	1152	–
	362	–	616	–	655	–	785	–	1108	–	1329	–
	417	–	–	–	–	–	–	–	–	–	–	–

solids was used and resulted in a concentration of 31 mg/L of aluminum and 28 mg/L of silicon. For gibbsite, 0.077 g was used, resulting in an aluminum concentration of 417 mg/L.

These solutions were filtered through a 0.45-μm nylon filter, and 13 mL of each was used to test the growth of uranium on NAS particles. For each NAS form, two vials were prepared. One, comprised of only the presaturated SRS blank solution, was used as the test blank, while the other also received 75 μL of a 10,000-mg/L uranium solution to provide a final concentration of 50 mg/L of uranium in the solution. Finally, the NAS solids were introduced in the vials (see details in Table 2.2). The vials were tightly closed and transferred to an 80° C shaker water bath, where they remained for a period of 4 days. At the end of the test, the samples were allowed to cool at room temperature and then were filtered through a 0.45-μm nylon filter. The filtrate solutions were analyzed by ICP-AES to evaluate the amount of uranium remaining in the solution after exposure. The solids were rinsed with deionized water to remove the excess salts. The rinse water was also analyzed by ICP-AES to verify that uranium was not lost during the rinse stage. The solids were allowed to dry before being prepared for scanning electron microscopy (SEM) examination. The powders were then placed on an SEM specimen stub, coated with gold, and examined by SEM with regular secondary electron (SE) imaging, energy dispersive spectroscopy (EDS) analysis, and back-scattering electron (BSE) imaging.

2.2.1.3 Preparation of NAS Coatings on Stainless Steel Foils

The work investigating the incorporation of uranium onto NAS coatings was conducted in two stages. The first stage was designed to produce well-characterized samples of NAS coatings of the identified phase on stainless steel surfaces. This was conducted in a manner similar to that used in the surface deposition tests conducted in FY 2001.[7] Results of that work indicate that it should be possible to reproducibly generate stainless steel coupons that have at least a partial coating of zeolite A, sodalite, cancrinite, or a combination of two phases. Solids are formed on stainless steel foil or coupon surfaces under a range of silicon and aluminum concentrations, temperatures, and reaction times. Stainless steel (304) foils were used in the tests. Silicon and aluminum solutions were prepared in a similar manner to that used in previous tests[7]; sodium metasilicate was the silicon source, and aluminum nitrate was the aluminum source. The NAS deposition on coupons are performed in capped Teflon containers. Figure 2.1 shows a schematic setup for heterogeneous growth of NAS coating on the bottom surface of a bent stainless steel foil, which is of interest for next-stage exposure to uranium-containing solutions. The preparation conditions are adjusted with regard to phases produced, amount of solids, and consistency in results.

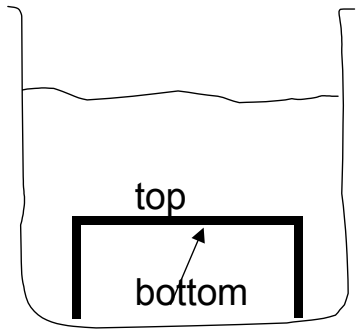


Fig. 2.1 Schematic of the bent stainless steel, facing down, submerged in NAS solution in a Teflon vessel.

The solution used for growing NAS coatings contained 0.133 *M* Al, 0.133 *M* Si, 4.15 *M* OH^-, 1.07 *M* NO_3^-, 0.67 *M* NO_2^-, and 5.89 *M* of total Na^+. This solution was prepared by mixing two

Table 2.2. ICP-AES results (mg/L) obtained after additions of NAS solids from Addai-Mensah[6] in the SRS simulant solution[a,c]

	Zeolite A [A1] = [Si] = 213[b]		Amorphous NAS [A1] = 124, [Si] = 120[b]		Sodalite [A1] = 139, [Si] = 133[b]		Cancrinite [A1] =31, [Si] = 28[b]		Gibbsite [A1] = 417[6]	
	Vial A1	Vial A2	Vial B1	Vial B2	Vial C1	Vial C2	Vial D1	Vial D2	Vial E1	Vial E2
Composition										
Background solution (mL)	13	13	13	13	13	13	13	13	13	13
NAS (g)	0.098	0.098	0.098	0.101	0.100	0.098	0.102	0.098	0.103	0.107
ICP-AES analysis										
Aluminum	262.7	267.6	286.8	286.4	290.3	289.0	176.8	176.1	2877	3076
Potassium	18.6	17.8	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0
Sodium	148,351	144,391	146,139	146,351	145,161	143,494	144,540	145,538	143,718	143,957
Silicon	294.3	296.1	283.1	283.6	269.9	269.3	165.5	163.9	<2.0	<2.0
Uranium	<1.50	30.89	<1.50	30.60	<1.50	32.48	<1.50	21.58	<1.50	5.56
Uranium in rinse solution	<0.03	1.23	<0.03	1.10	<0.03	2.46	<0.03	1.15	<0.03	0.30

[a]NAS solids were obtained form Dr. Addai-Mensah, University of South Australia.
[b]Concentration of background solution (mg/L).
[c]SRS simulant solution consists of SRS blank solution with some dissolved solids of corresponding phases.

equal volumes of stock solutions: Al-Stock (0.266 *M* Al, 4.15 *M* OH^-, 1.07 *M* NO_3^-, 0.67 *M* NO_2^-, and 5.09 *M* of total Na^+) and Si-Stock (0.266 *M* Si, 4.15 *M* OH^-, 1.07 *M* NO_3^-, 0.67 *M* NO_2^-, and 6.42 *M* of total Na^+). The Teflon vessels containing solutions and bent foils (initially at room temperature, ~ 23º C) were placed in an oven at 100º C. At prespecified times, a vessel was removed from the oven and cooled rapidly by immersion in tap water. The NAS-coated foil was then removed from the vessel and rinsed with deionized water. Thick NAS solid layers formed on the upper surfaces of the metal foils due to settlling and deposition of bulk NAS particles. That material was scraped off by using a razor blade. The NAS coatings on the bottom surfaces were examined by SEM (SE, EDS, and BSE) and X-ray diffraction (XRD).

2.2.1.4 Growth of NAS Coatings on Stainless Steel in the Presence of Uranium

An additional experiment was conducted similar to those above, but with uranium present in the starting solution. The NAS solution described above was spiked with 100 ppm uranium (source: 10,000 ppm uranium standard in nitric acid) and then contacted with stainless steel foil at 100˚ C for 24 h. The coating surface of the bottom was examined by SEM. As a control test, solution containing 100 ppm uranium (but no aluminum or silicon) was contacted with stainless steel foil at 100º C for 24 h.

2.2.1.6 Exposure of NAS Coatings to Uranium-Containing Solutions

For investigation of uranium incorporation onto preexisting NAS films, samples of stainless steel foils/coupons were coated with aluminosilicates of various phases (e.g., amorphous, zeolite A, sodalite, cancrinite). The samples were then contacted with uranium-containing simulant solutions (0, 25, and 50 ppm uranium) at 80˚ C for 24 h. The solutions, which had a composition of 6 *M* Na^+, 4.0 *M* OH^-, 1.0 *M* NO_3^-, and 1.0 *M* NO_2^-, were presaturated at room temperature with NAS corresponding to each phase (amorphous, zeolite A, sodalite, or cancrinite). After contact with the solution, the samples were then rinsed thoroughly with deionized water. The coating surfaces were analyzed by SEM and XRD:

- SEM/EDS analysis was used for solids morphology, mapping the location of uranium, and elemental analysis. These tests provide valuable information, including evidence of phase transformation, indication of uranium deposition, and distribution of uranium on the surface.
- XRD analysis was used for verification of the solid phases present and to determine if any NAS phase transformation occurred under the exposure conditions.

The quantity of coating material on the coupons was insufficient to obtain reliable quantitative values for uranium inclusion via dissolution and ICP-AES analysis.

2.2.2 Growth of NAS on Uranium

To investigate growth of aluminosilicates on uranium-containing solid particles, simulant solutions containing uranium were aged to precipitate uranium powder solids. The solutions were then spiked with known concentrations of aluminum and silicon and held at the temperature of interest. The growth of NAS on the surfaces of uranium powder solids was observed by SEM.

2.2.2.1 Preparation and Characterization of Uranium-Powder Solids

A solution was prepared combining 90 mL of 10% HNO_3 and 90 mL of a 10,000-mg/L ICP-AES standard solution (J. T. Baker "Baker instra-analyzed" plasma standard, lot L36430). This solution was stirred, and a 12.5% NaOH solution was used for neutralizing the acidic solution. At pH values of ~ 4-5, the precipitation began. The color of the solution changed from yellow at the beginning of the precipitation to dark orange at the end of the process. The precipitation was performed with an excess of NaOH to ensure that all uranium would precipitate. The crystals that formed settled very quickly on the bottom of the beaker. The supernatant was removed, and the slurry was centrifuged in order to remove the excess salts resulting from the neutralization. After centrifugation, the salts were rinsed with deionized water and centrifuged; the supernatant was then removed. This operation was performed three times to remove the excess salts. The centrifuged solids were transferred to an oven at 66º C for drying. After several hours, the uranium solids were removed from the oven and transferred into a vial. The amount of precipitated uranium salt/compound powder solids (i.e., uranium-powder solids) prepared was ~2.4 g. These solids were analyzed by XRD.

2.2.2.2 Stability of Uranium Particles in the Background Solution

A test was conducted to verify if the precipitated uranium compound powders were soluble in the SRS background solution (4 *M* NaOH + 1 *M* $NaNO_3$ + 1 *M* $NaNO_2$). A known quantity of uranium powders (~0.2 g) was placed into an Oak Ridge centrifuge tube with 20 mL of the background solution. The mixture was heated in an 80˚ C shaking water bath for 24 h. At the completion of the test, the tubes were removed from the water bath and allowed to cool to room temperature. The samples were then filtered through a 0.2-µm nylon filter. The solids were washed with deionized water to remove the excess salts from the background solution and then dried at 66º C for 24 h. The filtrates were analyzed by ICP-AES. The concentrations of uranium found in the filtrates were 14.23 and 15.36 mg/L. These numbers likely correspond to a slight dissolution of the uranium salts, with a possible contribution from uranium particles smaller than 0.2 µm.

2.2.2.3 Surface Precipitation of NAS on Uranium Powder Solids

For this test, samples were prepared in quadruplet. Two sets of samples were prepared: one set contained the NAS solution only, while the other contained the NAS solution and ~ 0.2 g of precipitated uranium salt/compound powder solids. In each tube 10 mL of stock aluminum solution (0.08 *M* $Al(NO_3)_3 \cdot 9H_2O$ + 1 *M* $NaNO_3$ + 1 *M* $NaNO_2$ + 4 *M* NaOH) and 10 mL of stock silicon solution (0.08 *M* $Na_2SiO_3 \cdot 5H_2O$ + 1 *M* $NaNO_3$ + 1 *M* $NaNO_2$ + 4 *M* NaOH) were added. The silicon and aluminum concentration in the mixed solution was 0.04 *M*. Approximately 0.2 g of uranium powder solids was introduced to each of four tubes, which is approximately three times the mass of NAS solids that would be expected to form under the experimental conditions. The tubes were transferred into the 80˚ C shaker water bath at for 24 h. The samples were then removed from the water bath, allowed to cool to room temperature, and filtered through a 0.2-µm nylon filter. The solids were rinsed three times with deionized water, with centrifugation

after each rinse, to remove the excess salts from the NAS solution and then dried at 66º C for 24 h. The filtrates were analyzed by ICP-AES. The results are presented in Table 2.3. The dried solid powders were examined by SEM (SE imaging, EDS analysis, and BSE imaging).

Table 2.3. ICP-AES analyses of the filtrates from the exposure of uranium particles to NAS solution

	With uranium				Without uranium			
	Test 1	Test 2	Test 3	Test 4	Test 5	Test 6	Test 7	Test 8
Composition								
Al stock solution (mL)	10	10	10	10	10	10	10	10
Si stock solution (mL)	10	10	10	10	10	10	10	10
Uranium salt (g)	0.206	0.234	0.224	0.215	0	0	0	0
ICP-AES analyses								
Aluminum (mg/L)	347	309	327	315	422	401	464	443
Silicon (mg/L)	415	385	399	390	437	411	480	459
Uranium (mg/L)	19.7	21.7	19.9	21.0	< 3.0	< 3.0	< 3.0	< 3.0

3. RESULTS AND DISCUSSION

3.1 CHARACTERISTICS OF URANIUM SOLUTION AND SOLIDS

Uranium solutions (10, 50, 100 ppm) in a background of 6 *M* Na^+, 4.0 *M* OH^-, 1.0 *M* NO_3^-, and 1.0 *M* NO_2^- are not thermodynamically stable. ICP-AES analysis indicated that the uranium concentration in the two solutions decreased to approximately 10 ppm after aging at room temperature for 24 h. Meanwhile, yellowish compounds precipitated/salted out of the solution and settled at the bottom. Heating the solution at 80° C further enhanced the aging and precipitation process. Some uranium precipitate solids were prepared by this aging method and analyzed by XRD, as shown in Fig. 3.1.

Uranium compound solids were also prepared by a chemical precipitation method. Uranium solution was neutralized by gradually adding NaOH solution (12.5%). The uranium compound powder solids produced by the neutralization method were analyzed by XRD (Fig. 3.1). Several sodium uranium oxides fit well to the somewhat broadened peaks (probably due to existence of nanocrystalline and amorphous phases): Na_2UO_5, $Na_2U_{2.5}O_{8.5}$, $Na_2U_2O_7$, some amorphous materials, and a few other unidentified minor ones.

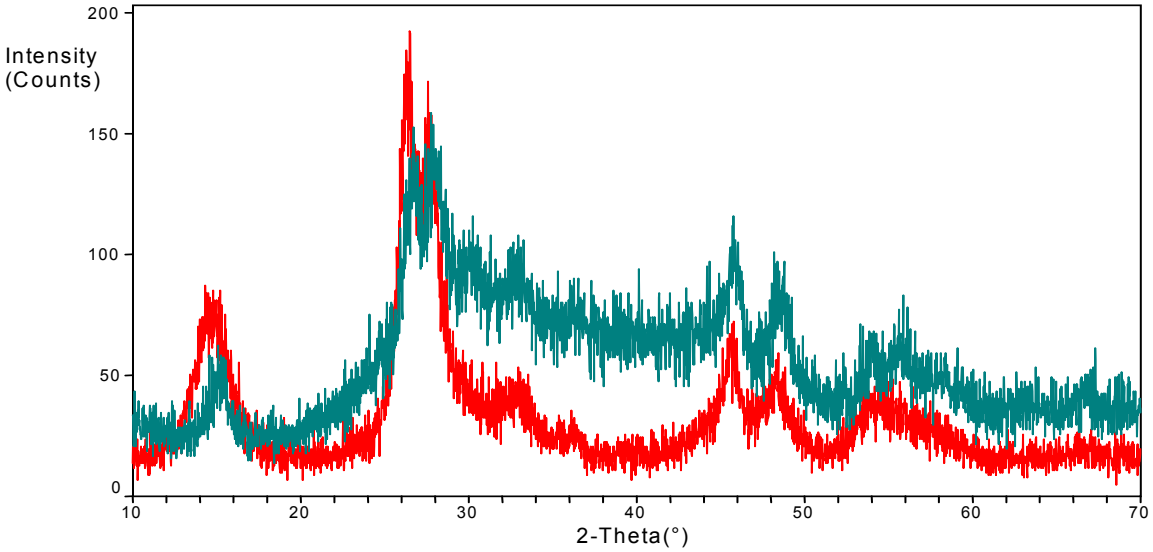


Fig. 3.1 XRD spectra of solids obtained from uranium solution. *Upper plot*: Solids from room-termperature aging of 100-ppm uranium solution: *lower plot*: Solids from NaOH neutralization of 1000-ppm uranium solution.

3.2 GROWTH OF URANIUM ON SURFACES OF NAS-POWDER SOLIDS

The NAS powder solids of various pure materials (amorphous, zeolite A, sodalite, and cancrinite) prepared by Addai-Mensah[6] were contacted with uranium-containing (50-ppm) solutions at 80°C for 24 h. Under such conditions, it is known that heating induces precipitation of uranium compounds in the NAS-free solutions (Section 3.1). In the presence of NAS particles and the presaturated aluminum and silicon concentrations (at room temperature), uranium ions appear to precipitate out of solution and uranium precipitates are mixed into the NAS particles. This phenomenon is displayed in the micrographs presented in Figs. 3.2 through 3.5. Bright areas in the SEM/BSE images correspond to the existence of uranium in the solids.

3.3 GROWTH OF NAS COATINGS ON STAINLESS STEEL SURFACES

Photographs of NAS coatings grown at 100° C for various periods of time are shown in Fig. 3.6. Thick coatings comprised primarily of solids that formed in solution and then settled, and not adhered well to the metal were found on the upper surfaces of the foils. The uniform, partially transparent, thin coatings of NAS on the bottom surfaces of the coupons provide a well-controlled, heterogeneously grown material of value for studying the interaction of uranium with NAS surfaces. The XRD analyses of the bottom-surface NAS coatings are shown in Fig. 3.7. At 45 min of contact with the solution at temperature, an amorphous coating was obtained. At 1 h, pure zeolite A coating was grown on the stainless steel surface. At 100 min, 2 h, and 3 h, NAS coatings of mixed phases (zeolite A + sodalite) were obtained. At 24 h, the zeolite A phase disappeared, and a cancrinite coating was obtained.

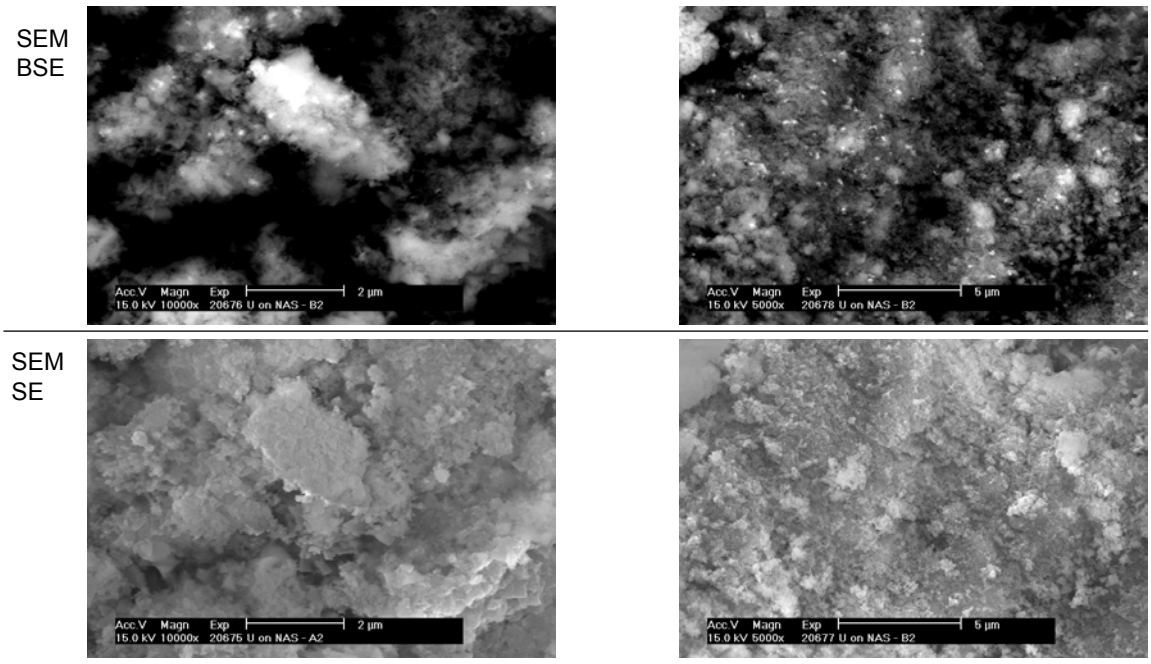


Fig. 3.2. Uranium precipitation on amorphous NAS powder solids.

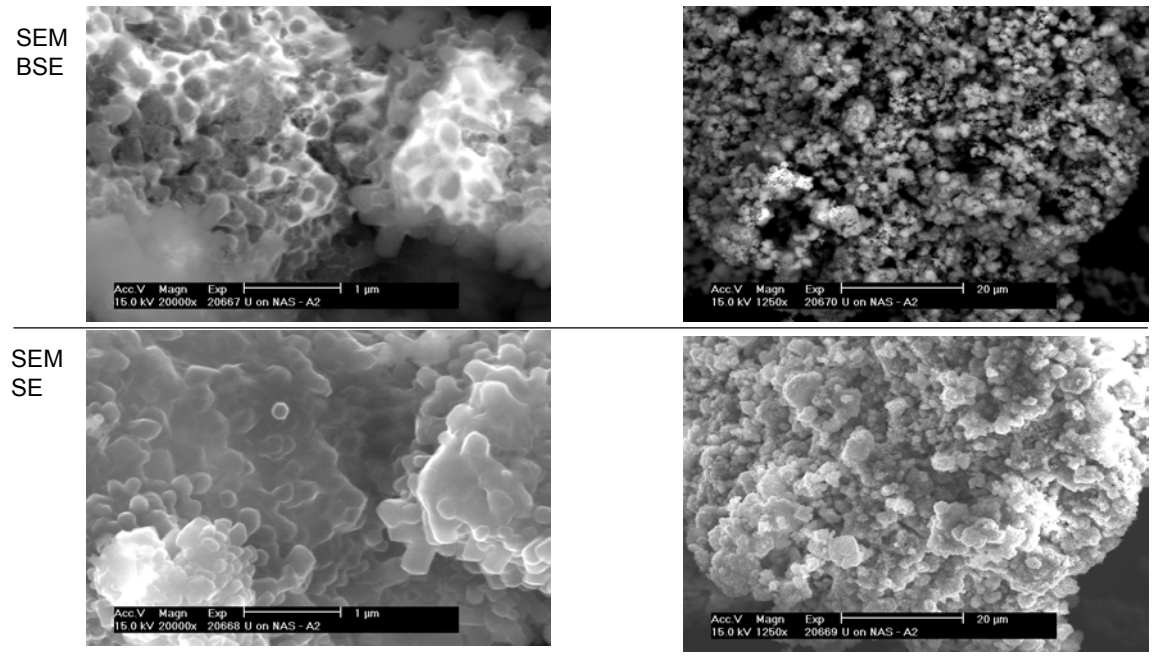


Fig. 3.3. Uranium precipitation on zeolite A powder solids.

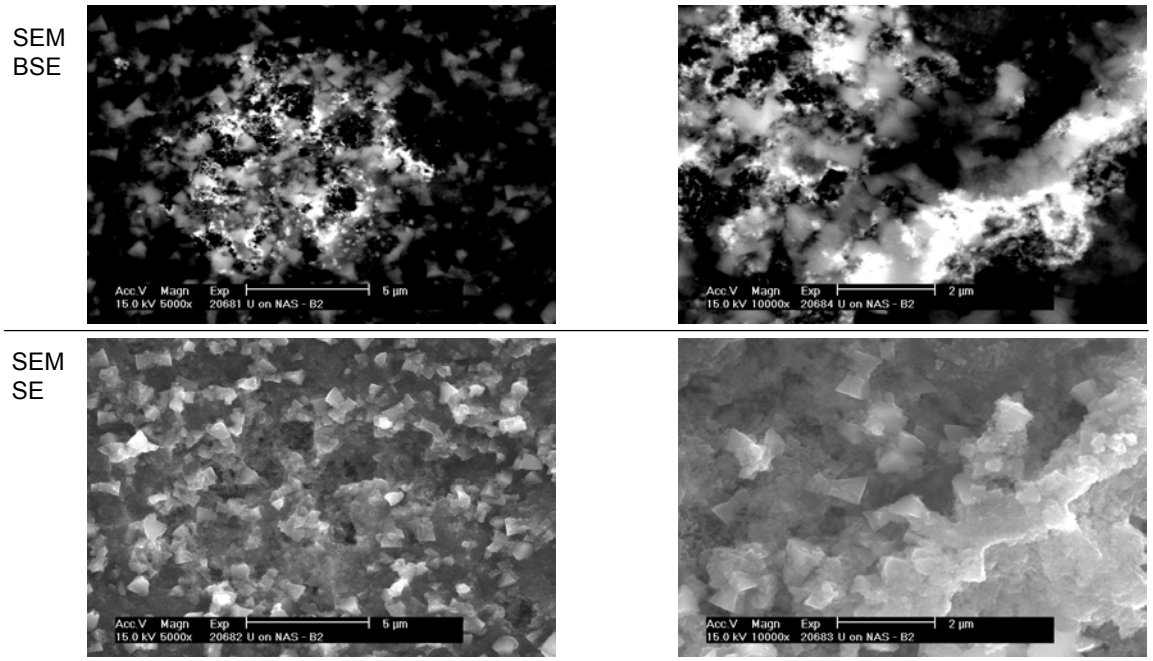


Fig. 3.4. Uranium precipitation on sodalite powder solids.

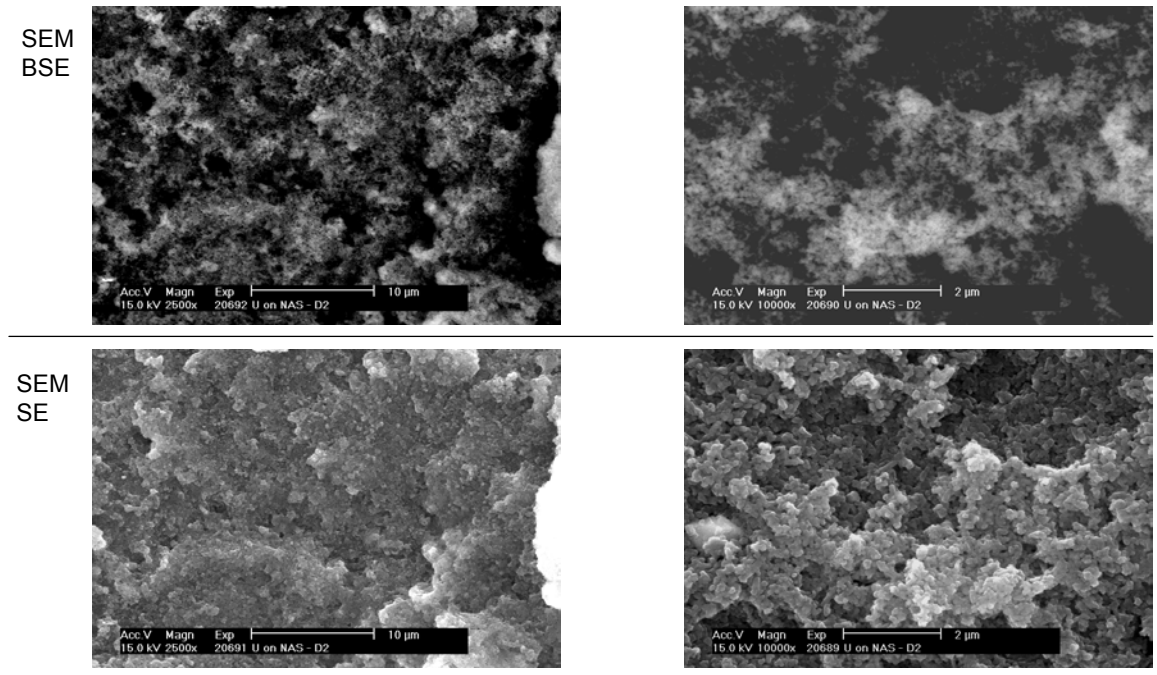


Fig. 3.5. Uranium precipitation on cancrinite powder solids.

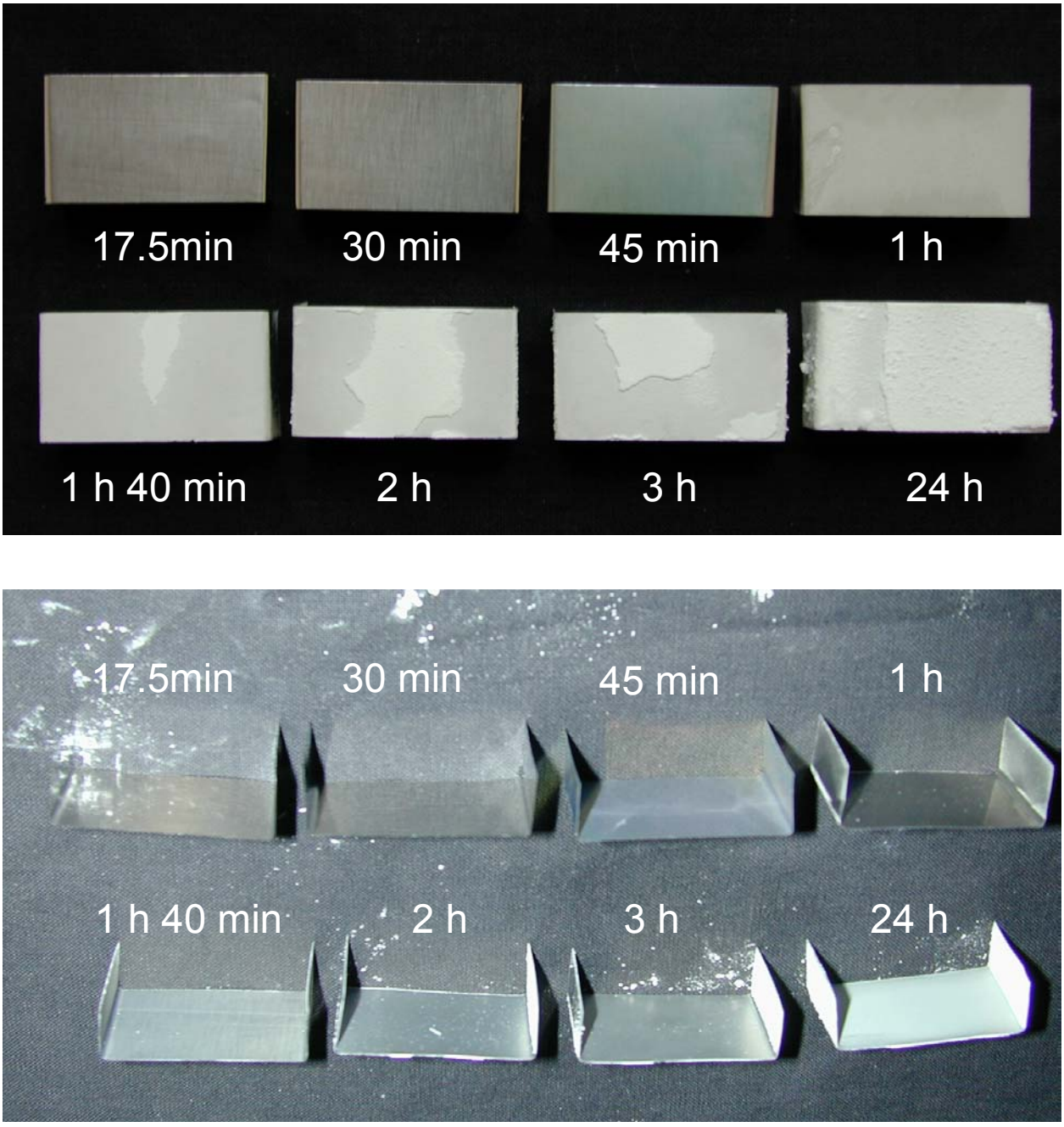


Fig. 3.6. NAS coatings grown at various time intervals. *Top*: upper surfaces of stainless steel foils; *Bottom*: bottom surfaces of foils.

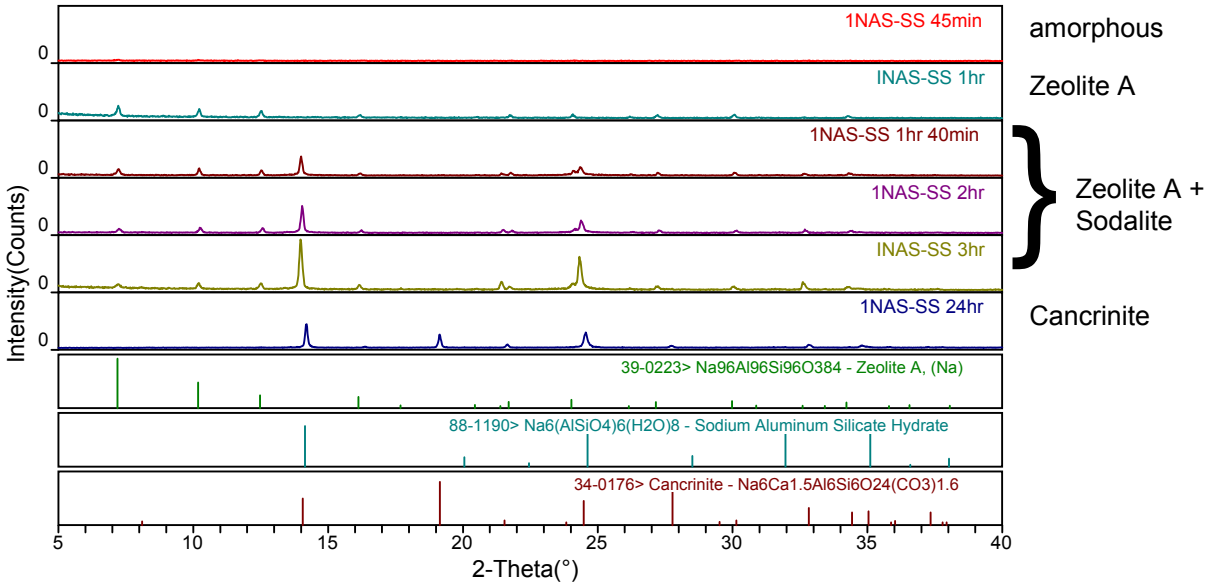


Fig 3.7. XRD spectra for NAS coatings obtained at various time intervals at 100°C.

SEM/SE images of NAS coating samples prepared at 100°C for different periods of time are shown in Figs. 3.8 through 3.14. For the first 30 min, no NAS coating is apparent on the foil surface, while NAS coatings are identified in subsequent samples. SEM images show the morphologies of the coatings as they progressed through phase transformations:
amorphous (45 min) →
zeolite A (1 h)→
zeolite A + sodalite (1 h 40min to 3 h) →
zeolite A + sodalite + cancrinite (5.5 h) →
sodalite + cancrinite (>9 h) →
cancrinite (24 h).

Unexpectedly, pure sodalite coatings could not be obtained via this procedure, because cancrinite phase forms before the zeolite A phase disappears. Addai-Mensah's procedure[6] for producing pure sodalite powders was also attempted, but no coating was grown on the stainless steel surface while all the particle solids formed in the bulk solution. Therefore, amorphous, zeolite A, and cancrinite coatings were used for the rest of the tests for contact with uranium solutions.

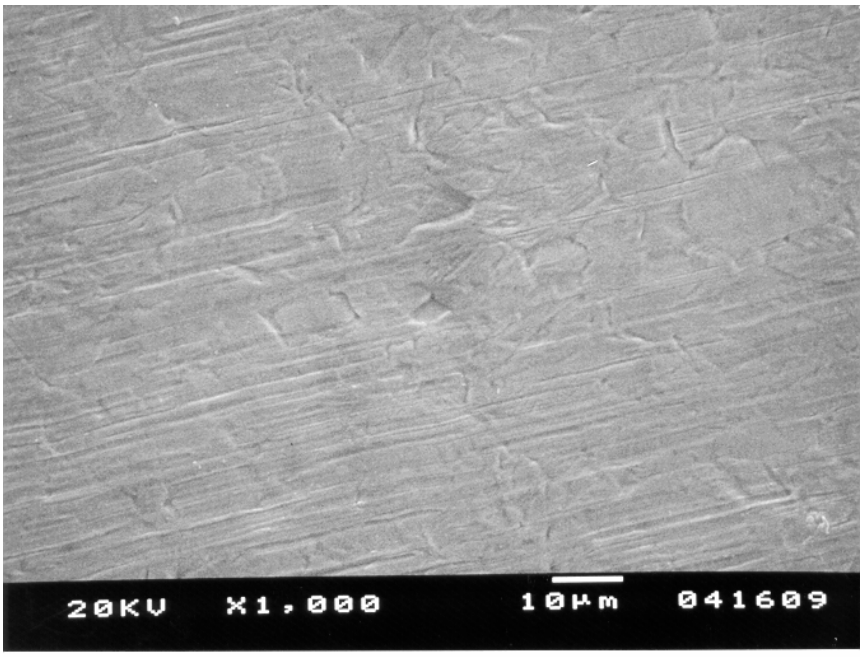


Fig. 3.8. Steel surface after 30-min exposure to coating solution at 100°C. No NAS coating was grown on the stainless steel surface.

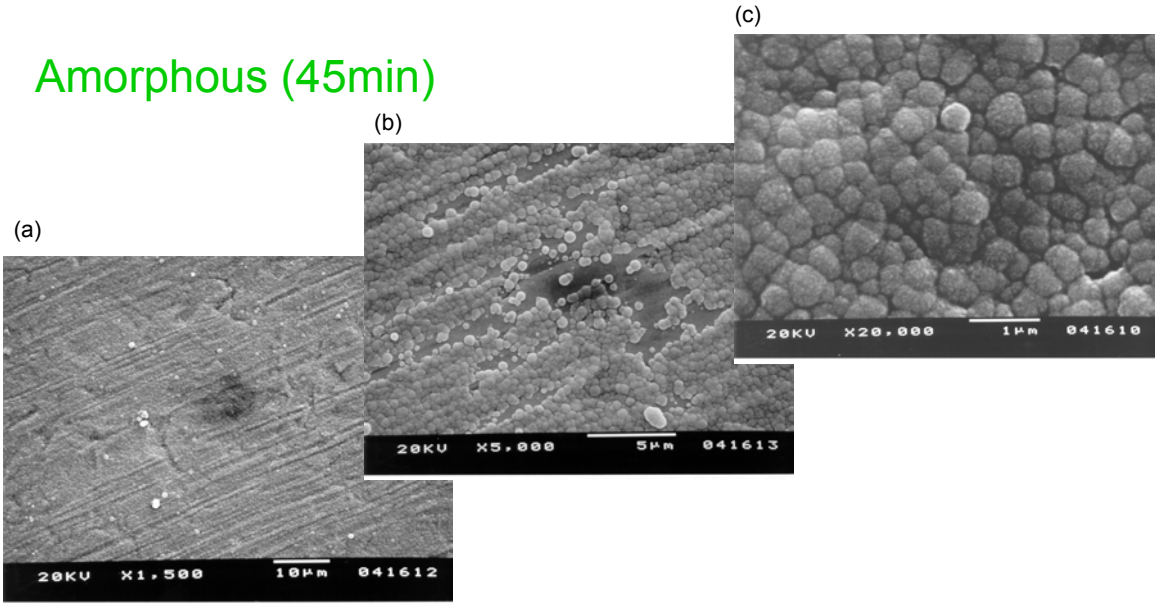


Fig. 3.9 Amorphous NAS coatings grown on stainless steel surface at 45 min. Three levels of magnification are shown**.**

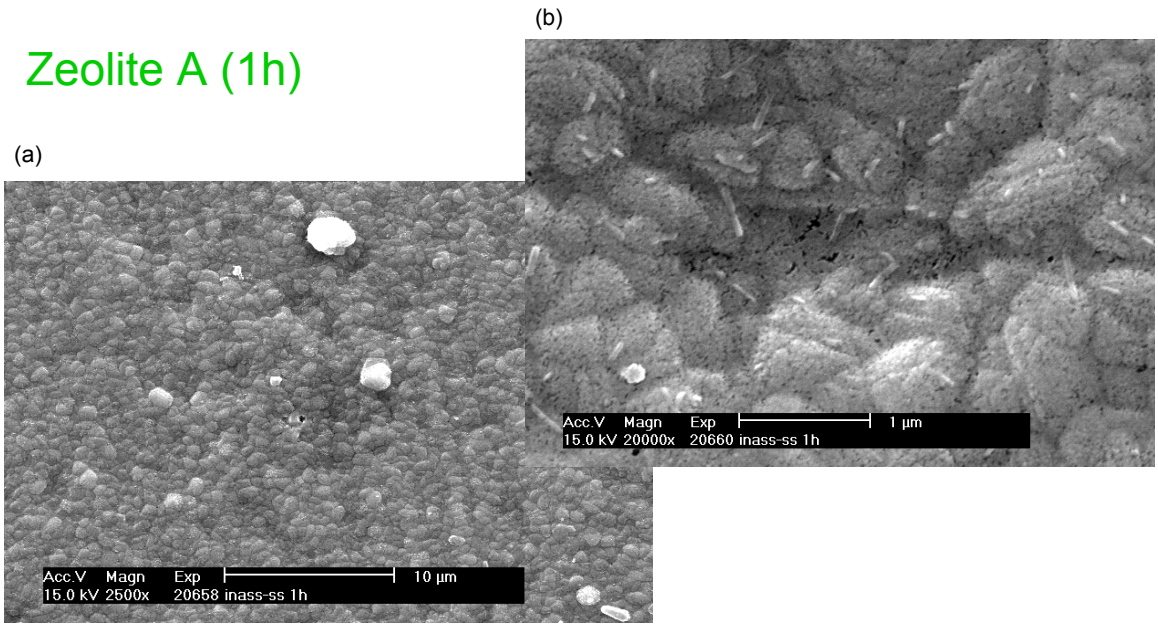


Fig. 3.10 Zeolite A coatings grown on stainless steel surface at 1 h. Two levels of magnification are shown.

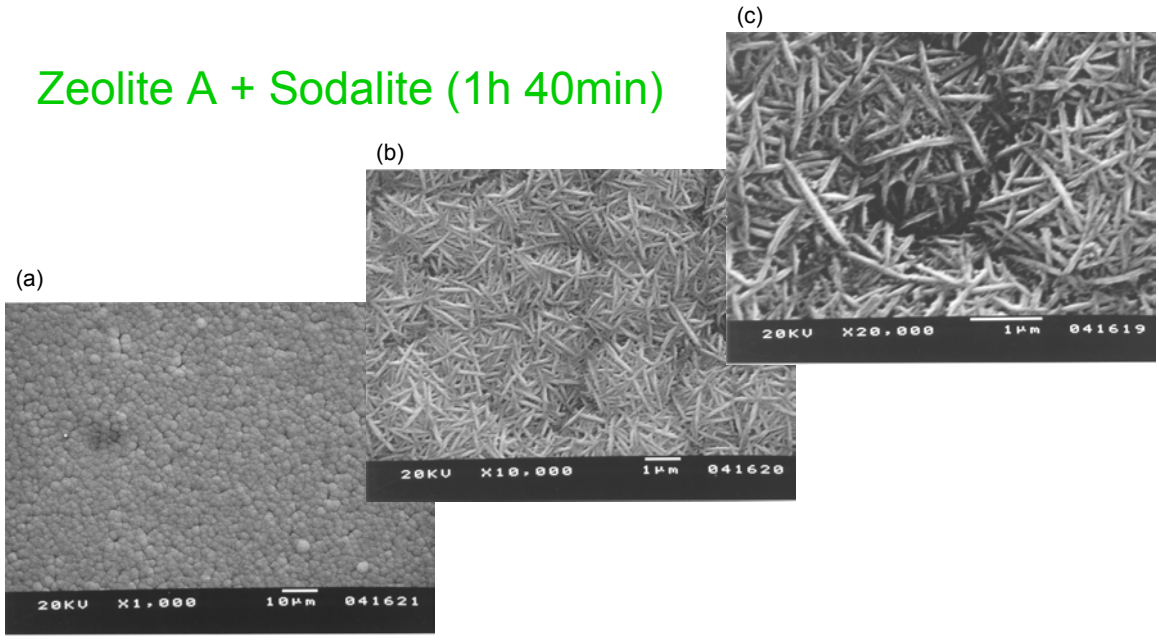


Fig. 3.11. Mixed-phase NAS (zeolite A + sodalite) coating grown on stainless steel surface at 1 h 40 min. Three levels of magnification are shown.

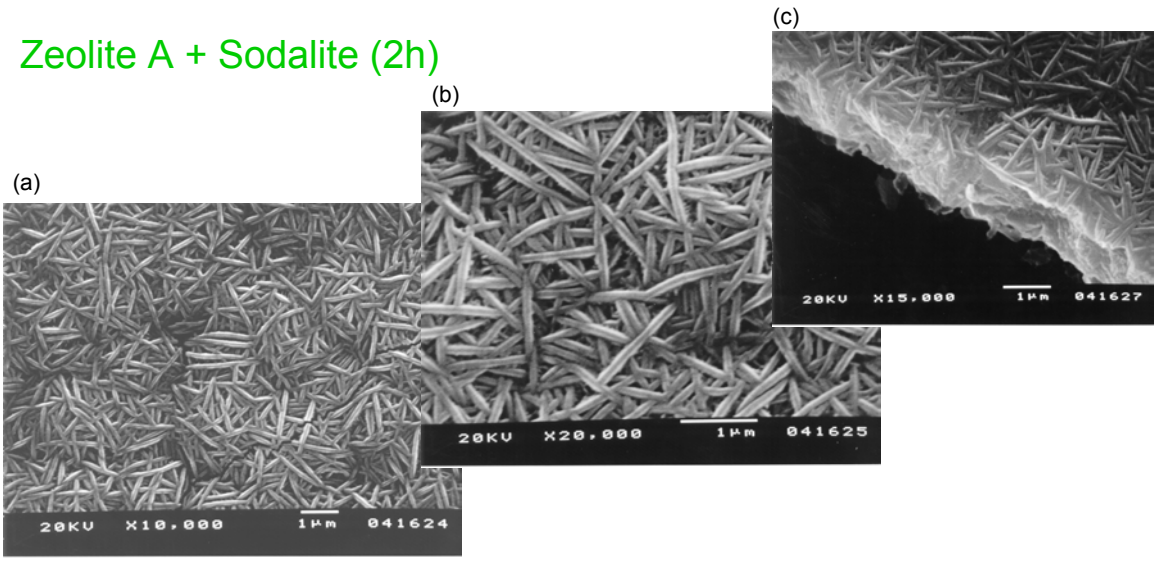


Fig. 3.12. Mixed-phase NAS (zeolite A + sodalite) coatings grown on stainless steel surface at 2 h. *(a)* **&** ***(b)*****:** Two levels of magnification of surface; *(c)* cross section of the coating.

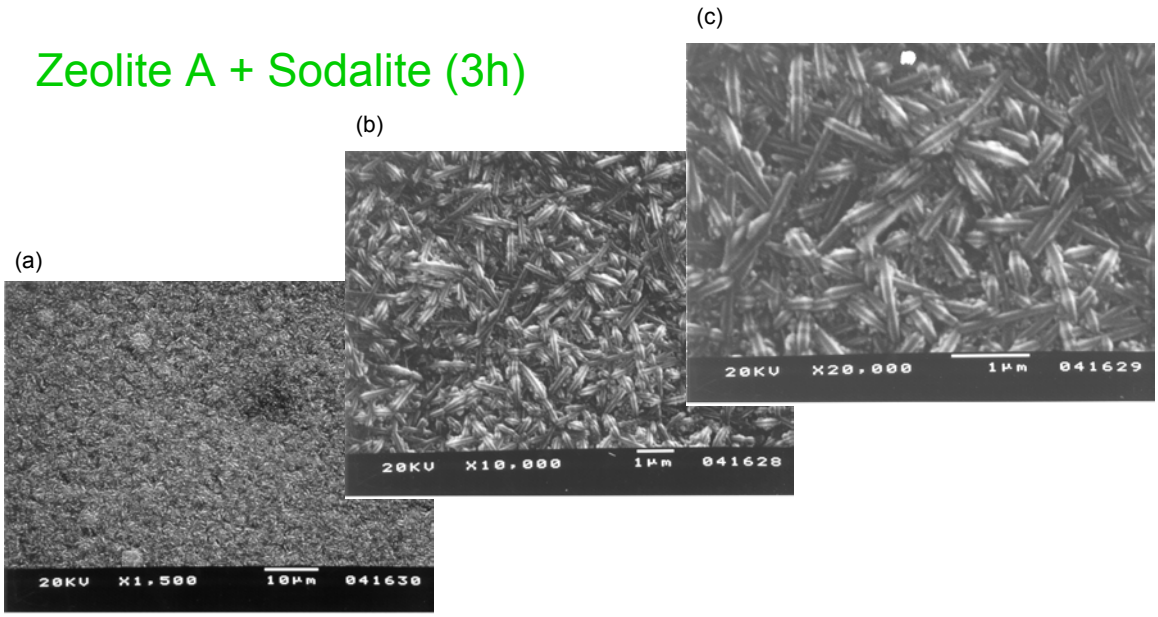


Fig. 3.13. Mixed-phase NAS (zeolite A + sodalite) coating grown on stainless steel surface at 3 h. Three levels of magnification are shown**.**

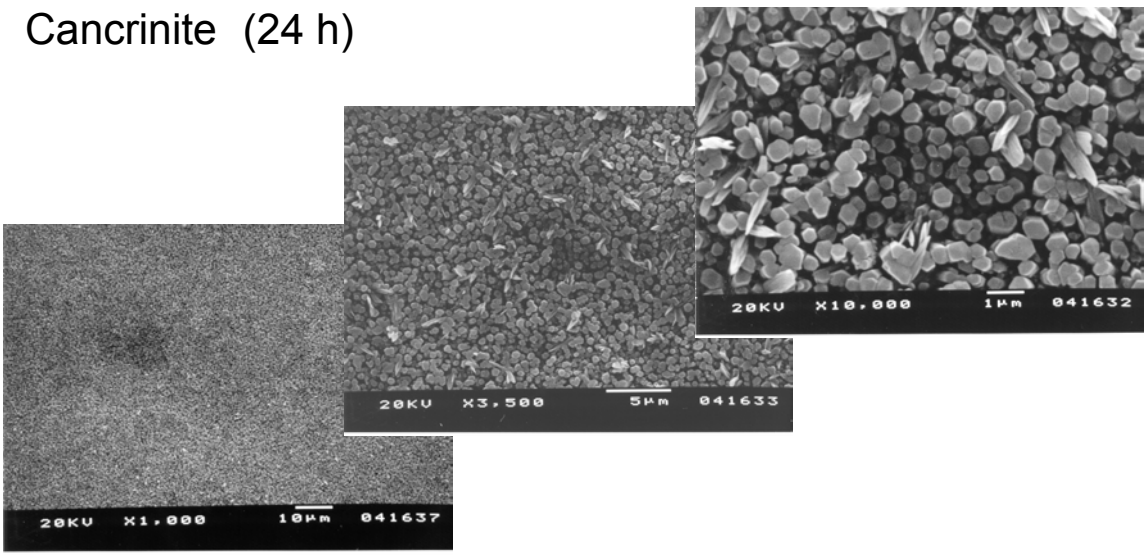


Fig. 3.14. Cancrinite coatings grown on stainless steel surface at 24 h. Three levels of magnification are shown.

3.4 SURFACE PRECIPITATION OF URANIUM ON NAS COATINGS

As a control test, bare stainless steel surfaces were exposed to 100-ppm uranium solution at 100°C for 24 h. Precipitation of yellow uranium compounds in bulk solution was observed. However, no uranium solids were grown on the bottom surface of the stainless steel foil, as shown in Fig. 3.15. This finding indicates that uranium compound precipitate does not grow directly on the bare steel surface, at least under the conditions of these experiments.

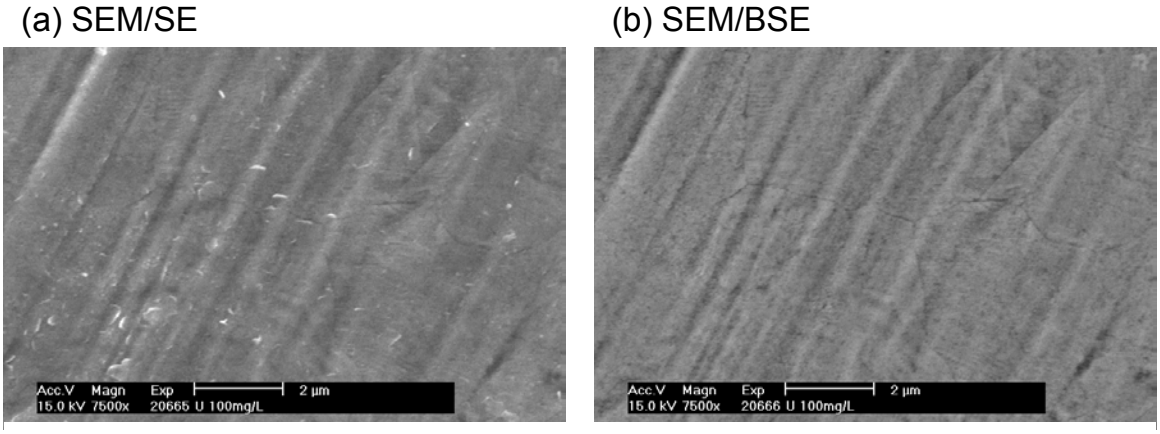


Fig. 3.15. Bare stainless steel surface after exposure to a 100-ppm uranium solution at 100° C for 24 h.

Another test was conducted under the conditions used to grow NAS coatings but with the soluble uranium present in the starting NAS solution. The solutions contained 0.133 *M* Al, 0.133 *M* Si, 4.15 *M* OH^-, 1.07 *M* NO_3^-, 0.67 *M* NO_2^-, 5.757 *M* of total Na^+ and soluble uranium (10,

50, and 100 ppm). After submerging the bent stainless steel foils, the solution was heated to 100°C for 24 h. SEM/SE images (Fig. 3.16) show that NAS (cancrinite) coating grew on the

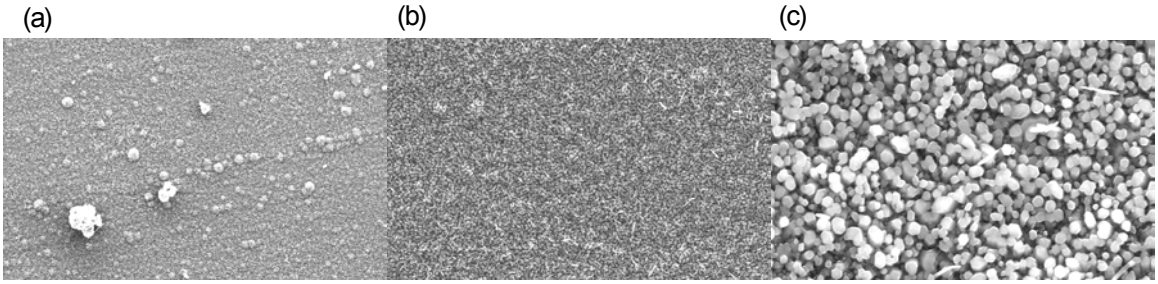


Fig. 3.16. NAS (cancrinite) coatings grown on stainless steel surface at 100°C for 24 h, in the presence of 100 ppm U in the starting solution. Three levels of magnification are shown.

surface of the bottom of the foil. However, no uranium was detected on the NAS coatings by SEM/BSE. In addition, XRD analyses (Fig. 3.17) of the coating surfaces did not indicate any presence of uranium compound phases in the NAS coating. Thus, uranium was not incorporated in the insitu grown NAS coatings under the conditions described here.

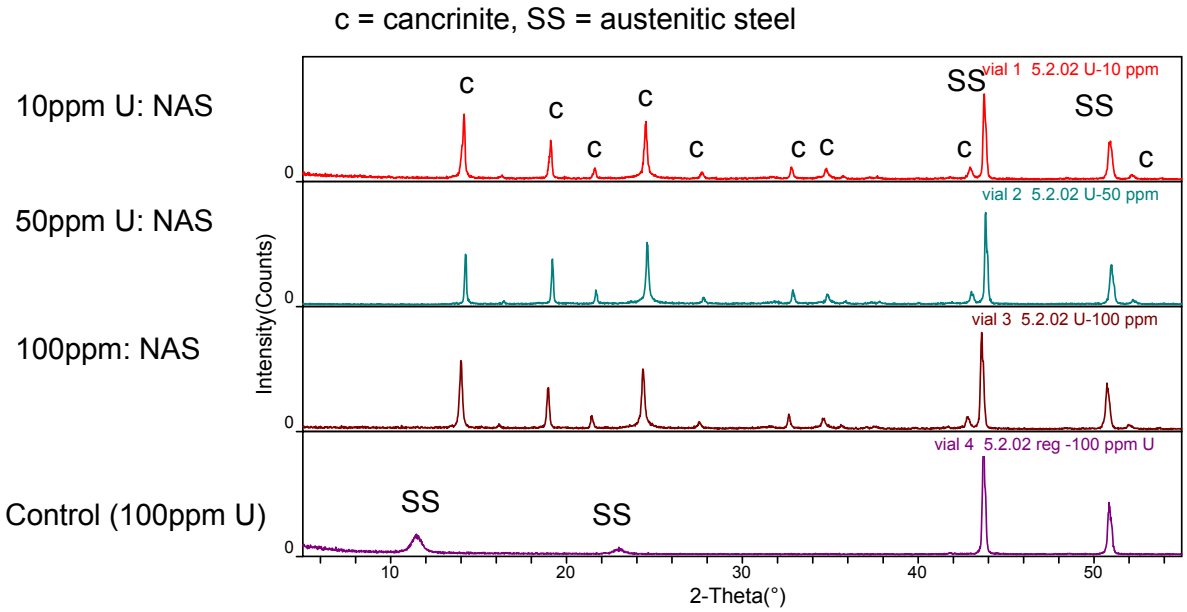


Fig. 3.17. XRD analyses of NAS coatings prepared in the presence of different initial concentrations of uranium.

Sample NAS coatings of amorphous, zeolite, and cancrinite phases grown on the bottom sides of the coupons were obtained for further contact with uranium solutions (0, 25, and 50 mg/L) that were presaturated with the corresponding NAS phases. SEM examinations (SE imaging, BSE imaging, and EDS spectrum) showed that uranium phases grow/deposit on the amorphous and cancrinite coating surfaces (Figs. 3.18 and 3.19). Bright white regions in the BSE images

correspond to the uranium-containing area. The EDS spectrum is used as a probe to confirm that the white bright areas show uranium spectral peaks. The results shown in Fig. 3.19(d) are particularly significant: the uranium solids appear to have grown in the crevices of the cancrinite solids. These results confirm that precipitation of uranium solids can occur on the surfaces of NAS solids. Possibility of uranium growth on zeolite A and sodalite cannot be excluded.

In summary, under the conditions of these tests, uranium does not appear to grow on the bare stainless steel surface. No incorporation of uranium into the NAS coating apparently occured during heterogeneous growth of NAS on stainless steel surfaces, perhaps because the elevated concentration of uranium (100 ppm) may have favored homogeneous growth of uranium solids in solution prior to the 30 min required for the onset of NAS coating formation. It was determined that uranium can grow/deposit on preexisting NAS coating surfaces, both for amorphous and for cancrinite phases. In addition, NAS can grow on the surface of uranium powder solids. Therefore, from these studies of uranium growth on NAS, it appears that multiple mechanisms are possible for uranium incorporation in evaporator scale, including the following:

1. uranium or uranium–NAS aggregates (uranium trapped in NAS aggregate solids) that formed in the bulk solution deposit onto the surface of the NAS solids on the wall due to hydrodynamics and settling, and
2. uranium solids heterogeneously grow onto NAS solids deposited onto the evaporator surfaces.

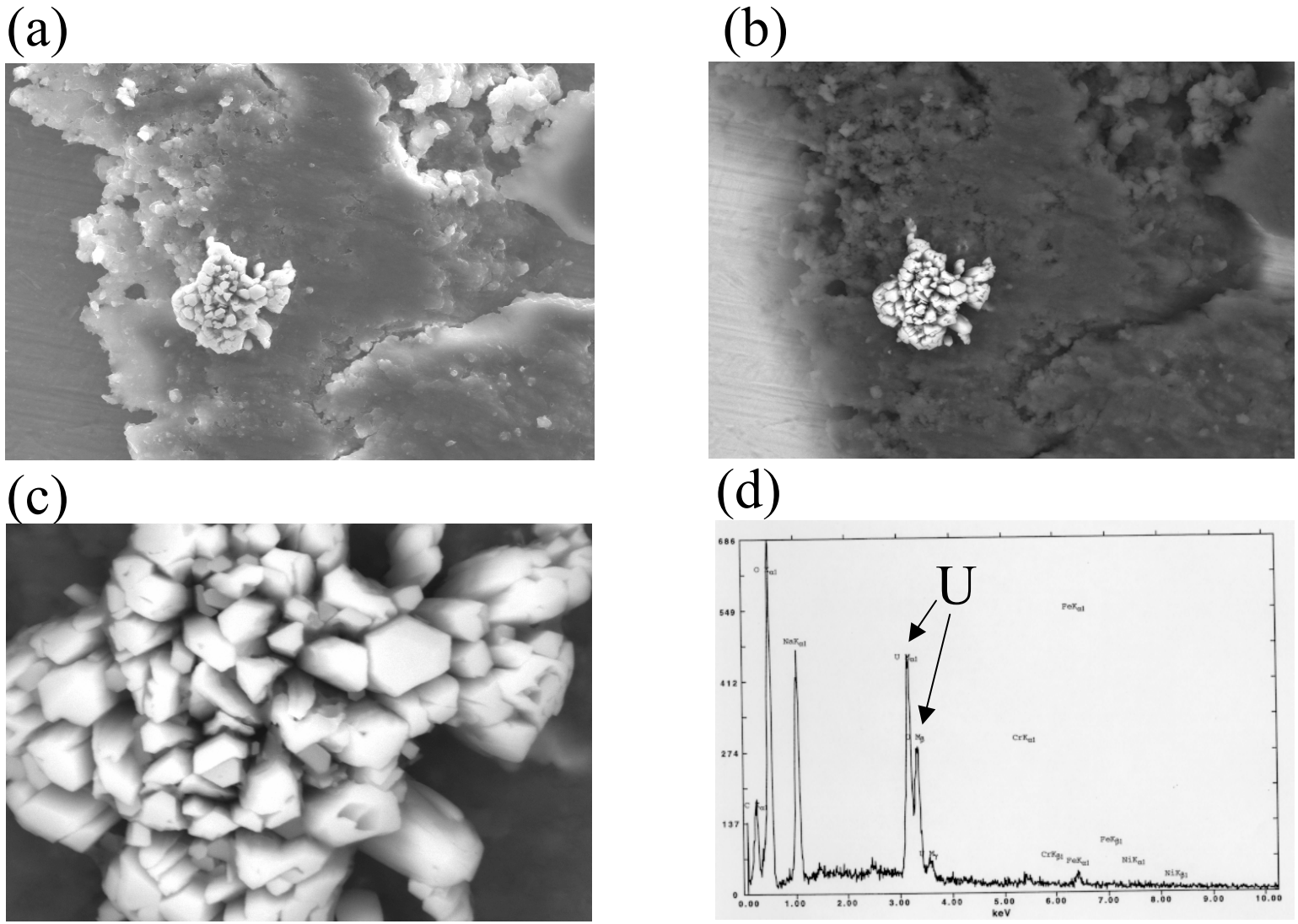
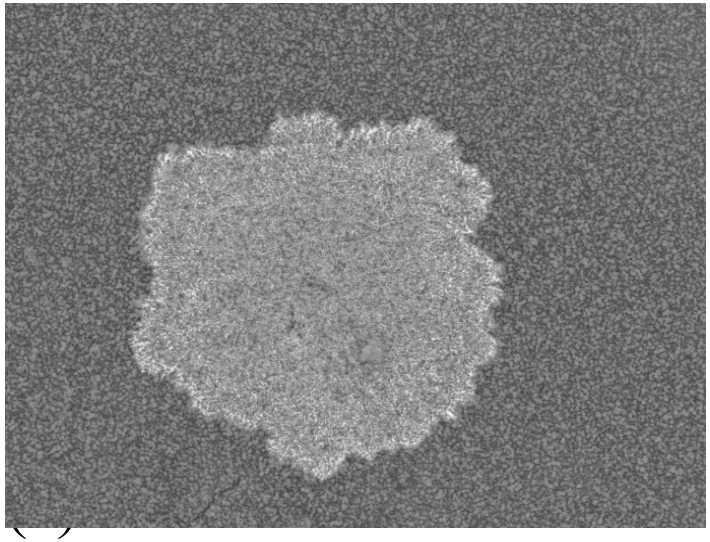
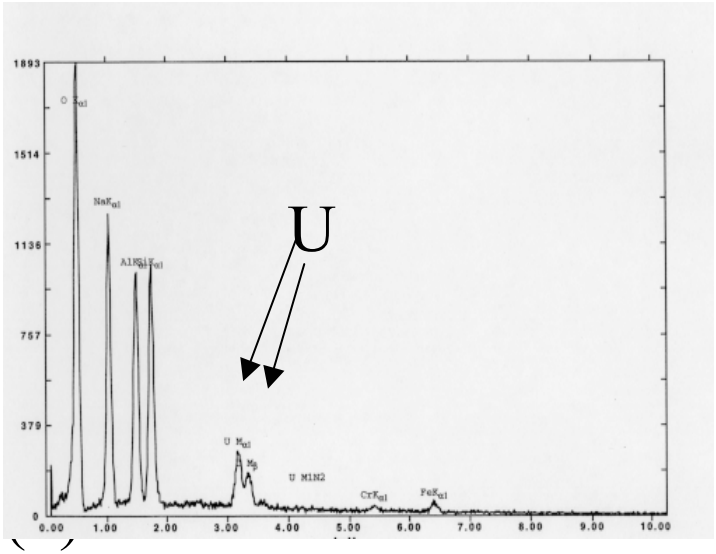


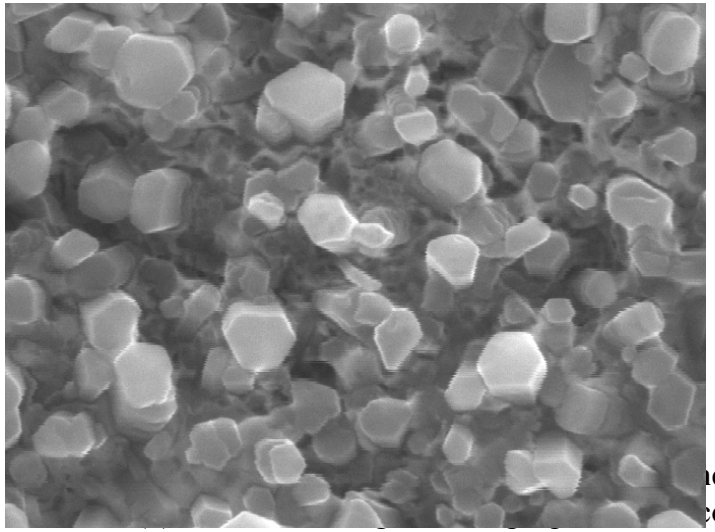
Fig. 3.18. Growth of uranium solids on the surface of amorphous NAS coating. *(a)* SEM/SE image; *(b)* SEM/BSE image of the same area as shown in *(a*); *(c*) Higher magnification of SEM/BSE image; *(d)* EDS analysis of the bright spot.

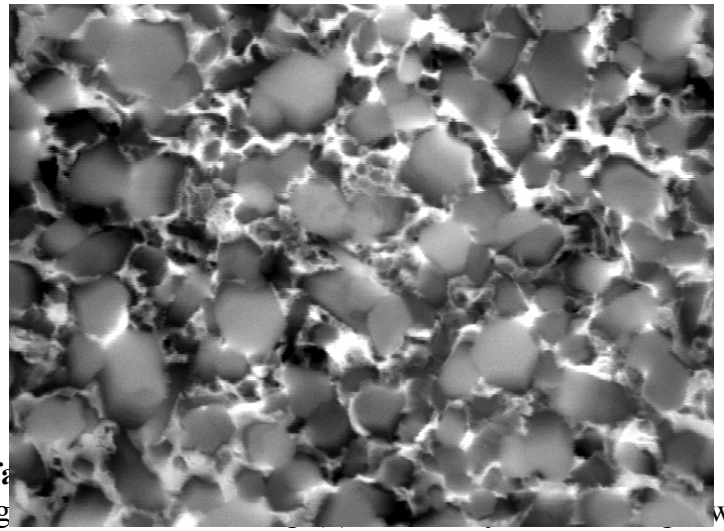
(a)

(b)









e surfa coverag white area. *(c)* SEM/S
image show details of the area containing uranium; *(d)* SEM/BSE
image of the same area as (c).

3.5 SURFACE PRECIPITATION OF NAS ON URANIUM POWDER SOLIDS

Uranium powder solids prepared by NaOH neutralization of acidic uranium solutions were then contacted with a NAS solution containing 0.04 *M* $Al(NO_3)_3 \cdot 9H_2O$, 0.04 *M* $Na_2SiO_3 \cdot 5H_2O$, 1 *M* $NaNO_3$, 1 *M* $NaNO_2$, and 4 *M* NaOH. These conditions induced the precipitation of NAS particles in the bulk solutions. Furthermore, NAS clusters/particles appear to have grown/deposited on the surfaces of uranium powder solids (Fig. 3.20). SEM/SE and corresponding BSE images clearly show that NAS cluster particles attached to the surfaces of uranium powder solids, which are polycrystalline mixed-phase sodium uranium oxides.

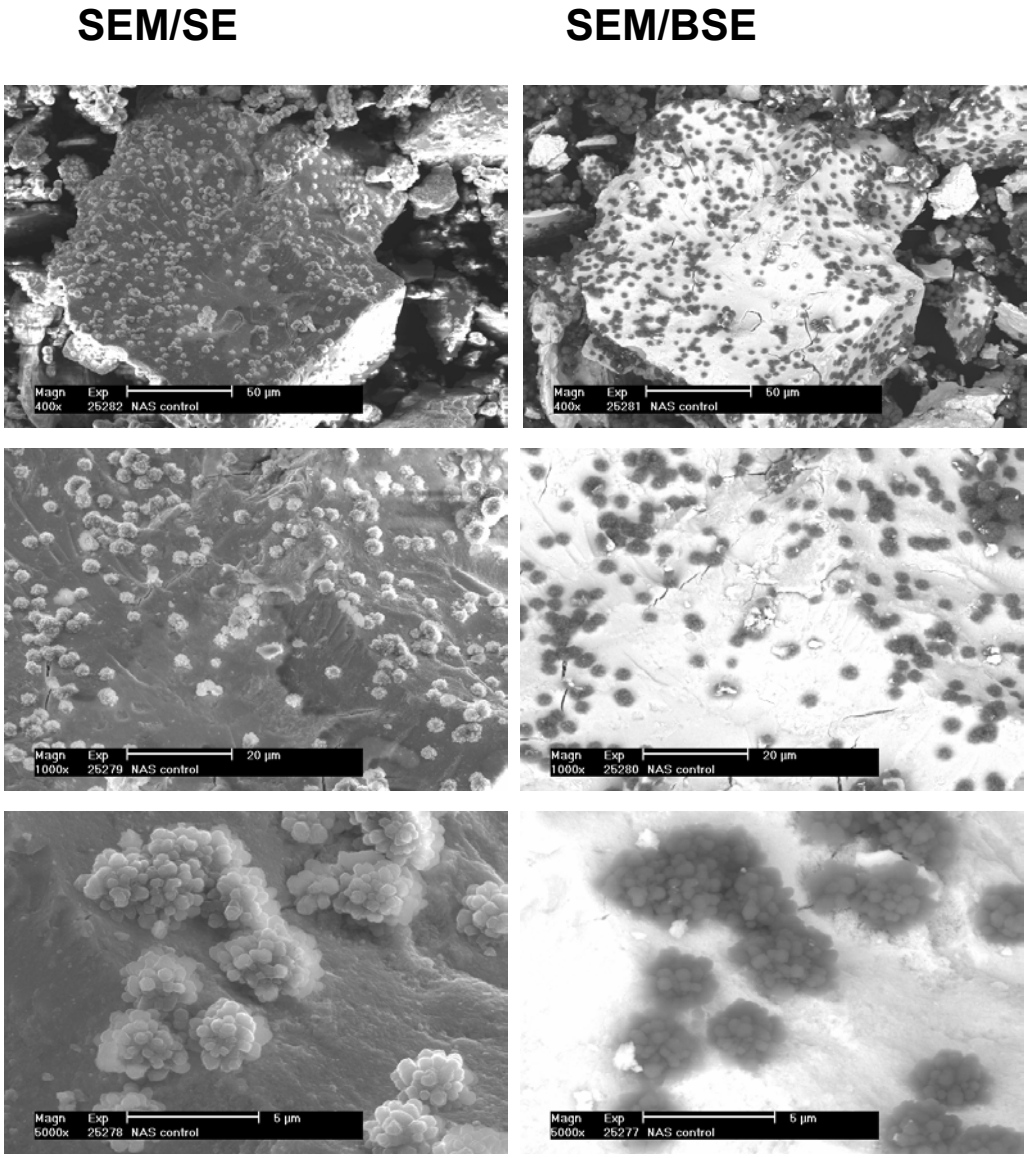


Fig. 3.20. Surface precipitation of NAS clusters/particles on uranium powder solids.

4. SUMMARY AND RECOMMENDATIONS

4.1 SUMMARY

Although qualitative in nature, the results of these surface precipitation tests demonstrate the following major points:

1. Under conditions of uranium compound precipitation in bulk solution, in the absence of NAS, uranium phase precipitation did not occur on bare stainless steel surfaces.
2. During insitu growth of NAS coatings on stainless steel surfaces in the presence of soluble uranium, uranium species were not incorporated in or grown/deposited on the NAS coating. However, because the experiments were conducted in batch mode, this finding does not preclude incorporation of uranium into NAS scale during growth.
3. When NAS powder solids of various pure phases (amorphous, zeolite A, sodalite, and cancrinite) were contacted with uranium solutions presaturated with the corresponding NAS phase, precipitated uranium appeared to aggregate with the preexisting NAS particles and become physically trapped in the NAS powder solids.
4. When NAS coatings of various phases (amorphous, zeolite A, and cancrinite) were contacted with uranium solutions, uranium solids were formed on the surfaces of amorphous and cancrinite coatings.
5. NAS clusters/particles can grow/deposit on the surfaces of uranium powder solids that are exposed to aluminum/silicon-containing solutions.

These tests have demonstrated that the mechanisms of uranium incorporation in the NAS solid scale of the 2H evaporator could be either uranium–NAS particle aggregation and encapsulation or surface growth/deposition uranium on NAS and/or NAS on uranium solid surfaces).

Particularly notable is the fourth-listed finding: uranium solids can form on existing NAS scale, including cancrinite solids. If NAS scale is present and uranium is in sufficient concentration in solution to precipitate, a portion of the uranium can be expected to become associated with the scale.

4.2 RECOMMENDATIONS FOR FUTURE WORK

These bench-scale tests have shown that uranium can be incorporated in NAS through encapsulation in bulk agglomerated NAS particles of different crystalline phases (amorphous, zeolite A, sodalite, and cancrinite) as well as through heterogeneous deposition on the surfaces of NAS coatings (amorphous and cancrinite) grown on stainless steel. In addition, NAS crystals were found to be able to grow on the surfaces of precipitated uranium solids. The data obtained to date on uranium–NAS affinity are qualitative. A necessary next step is to quantitatively determine the amounts of uranium that may be incorporated into NAS scale solids under various conditions (silicon/aluminum ratio, uranium concentration, temperature, and deposition time).

Continuous-flow bench-scale tests are recommended to determine the amounts of uranium and NAS in coatings grown on stainless steel surfaces under different operating conditions. In these studies, the deposited solid layers with incorporated uranium were too thin to permit accurate measurement of the quantities of Si, Al, and U in a reliable manner. A continuous-flow system feeding significant volumes of simulant containing U, Si, and Al through a vessel containing stainless steel coupons immersed in boiling solution would allow the formation of thicker films, thus enabling the determination of the solids composition. The results would be useful in planning pilot-scale evaporator testing, and the data would provide information to guide plant operations by estimating the magnitude of uranium incorporation in evaporator scale deposits formed under different operating conditions.

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